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Contributions from thermal lattice defects to the expansion of solid and liquid metals

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With 1 figure in the text

1. Introduction

As found by Grüneisen about fifty years ago the thermal expansion is at low temperatures proportional to the energy content and deviates at high temperatures from this proportionality towards higher expansion. For these phenomena there has for a very long time been a rather loose connection between the results of theoretical attempts and those of experiments. The present writer has made a re-examination of these and related phenomena on the basis of a phenomenological analysis of the experimental results combined with partly new assumptions concerning the sources of energy and expansion (1). In a recent paper (2) the energy content of solid Au, Ag, Cu, and Al was analyzed in detail. This analysis will now be followed by a discussion of the thermal expansion of the same metals including also the expansion at the melting point and in the liquid state.

2. The energy content

We shall first briefly recapitulate the results of the recent investigation (2) concerning the energy content of the metals Au, Ag, Cu, and Al in their solid state. It was shown that the total observable energy content per mole E_{obs}, obtained by integrating over the specific heat from absolute zero to a given temperature, can be described as a sum of four parts

$$E_{\text{obs}} = E_{\text{vib}} + E_{\text{el}} + E_{\text{I}} + E_{\text{II}}. \tag{1}$$

E_{vib} is the observable part of the energy due to vibrations of the atoms. The key to the dividing of the energy is the assumption that this observable energy of vibrations at high temperatures approaches the value

$$E_{\text{vib}} = 3\,R\,T - E_z \tag{2}$$

where E_z is the vibrational zero-point energy, which is not directly observable. This means that the sum of zero-point energy and thermal vibrational energy approaches the classical value $3\,R\,T$, R being the gas constant. At low temperatures equation (2) gives too small values for E_{vib}, which should reach zero at

$T = E_z/3\,R$. The difference between the real E_{vib} and that calculated from equation (2) is a quantity which was called the residual zero-point energy E_{zr} and which with increasing T passes from E_z to 0. The full expression for E_{vib} thus is

$$E_{\mathrm{vib}} = 3\,R\,T - E_z + E_{zr}. \tag{3}$$

E_{el} in equation (1) is the thermal energy of the free electrons.

E_{I} and E_{II} could be described as functions of the temperature by the expressions

$$E_{\mathrm{I}} = A_{\mathrm{I}} \exp\,(-H_{\mathrm{I}}/R\,T) \tag{4}$$

and

$$E_{\mathrm{II}} = A_{\mathrm{II}} \exp\,(-H_{\mathrm{II}}/R\,T) \tag{5}$$

where A_{I}, H_{I}, A_{II} and H_{II} are empirical constants. These expressions reveal the sources of the energies E_{I} and E_{II} to be thermal lattice defects. The order of magnitude of the heat of formation H_{II} is 1 eV and the corresponding defects are identified as vacancies. The order of H_{I} is 0.2 eV and the structure of these defects is still not established.

3. Assumptions concerning the thermal expansion of solid metals

As was first found by Grüneisen there is at low and medium temperatures a good proportionality between the increase of volume and the increase of energy with increasing temperature. At these temperatures the energy is predominatingly of vibrational origin and the thermal expansion is therefore proportional to E_{vib}. We now assume that the vibrational part of the expansion remains proportional to E_{vib} also at high temperatures. This proportionality also follows from considerations of the thermal density fluctuations (1). At high temperatures E_{vib} is described by equation (2), which means that the vibrational part of the expansion varies linearly with T.

We have no basis for a judging if the small electron energy E_{el}, which is proportional to T^2, has any influence on the thermal expansion. We shall try the assumption that an eventual influence is negligible.

The structural energy E_{I} most probably originates from some lattice defects and it is natural to assume a contribution to the expansion that is proportional to E_{I} as long as the number of defects is small.

The energy E_{II} most probably originates from vacancies with a heat of formation H_{II}. Their number pro mole is $E_{\mathrm{II}}/H_{\mathrm{II}}$. If each vacancy increases the volume in the same way as an added atom, the relative increase of volume due to vacancies should also be $E_{\mathrm{II}}/H_{\mathrm{II}}$. According to calculations by Eshelby (3) and Jongenburger (4) the real volume expansion should be smaller by a factor of 0.6, owing to relaxation of the lattice. As, however, these calculations are based on a static lattice, it is not obvious whether they also apply to the thermally agitated and defective lattice which may be expected at the temperatures where vacancies appear at an appreciable extent. We therefore prefer first to try the simple assumption that the relative increase of volume is equal to $E_{\mathrm{II}}/H_{\mathrm{II}}$.

Summing up we arrive at a tentative expression for the relative increase of volume which may be written

Table 1. Thermal expansion of solid *Au*.

Experimental data from Nix and MacNair (N. M.), Austin (A.), and Esser and Eusterbrock (E. E.).

$E_z = 351$, $A_{\mathrm{I}} = 2480$, $H_{\mathrm{I}} = 4530$, $A_{\mathrm{II}} = 1050000$, $H_{\mathrm{II}} = 23000$ cal/mole.

°K	$\frac{V-V_z}{V_0} \times 10_5$			$0.702\ E_{\mathrm{vib}}$	$1.65\ E_{\mathrm{I}}$	$\frac{10^5}{H_{\mathrm{II}}} \times E_{\mathrm{II}}$	$\frac{\Delta V}{V_0} \times 10^5$ obs − cal
	N. M.	A	E. E.				
100	221			205			+ 16
150	401			394			+ 7
200	596			593			+ 3
250	801			800			+ 1
273	900	900	900	896	2		+ 2
323	1113	1112	1113	1105	3		+ 5
373	1324	1328	1330	1314	8		+ 5
423	1535	1547	1550	1523	18		+ 3
473	1761	1769	1773	1733	33		+ 2
523	1984	1996	2000	1942	53		− 2
573	2222	2226	2231	2151	76		− 1
623	2465	2461	2465	2360	106		− 3
673	2703	2701	2705	2569	139		− 5
723	2945	2947	2950	2779	175		− 7
773	3193	3197	3199	2988	215	1	− 8
823	3455	3454	3454	3197	256	4	− 3
873	3719	3715	3714	3406	300	9	+ 1
923	3976	3983	3980	3615	347	17	+ 1
973	4240	4259	4253	3824	393	30	+ 4
1023		4542	4532	4034	441	57	0
1073		4830	4817	4243	488	96	− 10
1123		5127	5110	4453	538	157	− 37
1173		5431	5409	4662	586	239	− 78
1223		(5749)	5717	4871	634	361	−149

$$\frac{V-V_z}{V_0} = a\,E_{\mathrm{vib}} + b\,E_{\mathrm{I}} + \frac{1}{H_{\mathrm{II}}}\,E_{\mathrm{II}} \tag{6}$$

For practical reasons the difference between the volume V at a given temperature and the volume V_z at absolute zero is here taken relative to the volume V_0 at 0°C, which is the reference temperature for most dilatometric measurements. This choice of V_0 instead of V_z as reference value has an influence on the constants a and b of the order of one per cent. The last term in equation (6) gives the fraction of atoms replaced by vacancies. It is of course not rational to compare this fraction with the change of volume referred to the volume V_0 at 0°C. On the other hand it is difficult to say what should be most rational, a reference to V_z or to the volume expanded by the lattice vibrations. This makes an uncertainty of about 5 % which, however, does not matter as the present experimental uncertainty about the term due to vacancies will be found to be much larger than that.

For a comparison of equation (6) with experimental results concerning $(V-V_z)/V_0$ for Au, Ag, Cu, and Al we take E_{vib}, E_{I}, E_{II}, and H_{II} from the results of the

Table 2. Thermal expansion of solid *Ag*.

Experimental data from Esser and Eusterbrock (E. E.).

$E_z = 403$, $A_I = 4370$, $H_I = 5180$, $A_{II} = 891000$, $H_{II} = 27500$ cal/mole.

°K	$\frac{V - V_z}{V_0} \times 10^5$ E. E.	$0.97\ E_{vib}$	$1.6\ E_I$	$\frac{10^5}{H_{II}} \times E_{II}$	$\frac{\Delta V}{V_0} \times 10^5$
273	1187	1187	0		0
323	1480	1476	2		+ 3
373	1778	1765	7		+ 6
423	2078	2054	15		+ 9
473	2381	2343	29		+ 9
523	2691	2632	48		+ 11
573	3002	2921	75		+ 6
623	3317	3211	107		+ 1
673	3644	3500	146		− 2
723	3976	3789	192		− 5
773	4313	4079	242	1	− 9
823	4659	4368	296	2	− 7
873	5012	4657	355	4	− 4
923	5375	4946	418	10	+ 1
973	5747	5235	482	22	+ 8
1023	6130	5524	549	44	+ 13
1073	6524	5813	618	83	+ 10
1123	6929	6102	690	148	− 11
1173	7346	6391	758	247	− 50

earlier paper (2). The constants *a* and *b* thus are the only unknown quantities to be determined. The vibrational term with the constant *a* dominates at temperatures below and around room temperature. The term due to the primary defects with the constant *b* becomes important at elevated temperatures. The last term due to the vacancies appears at still higher temperatures and has no very great influence on the determination of *a* and *b*.

4. Comparison with experimental results

The experimental and calculated values for Au, Ag, Cu, and Al needed for a test of equation (6) are put together in the Tables 1 to 4. The volume expansions are calculated from the dilatometric measurements by Nix and MacNair (5) on Au, Cu, and Al in the range from − 180 to 700, 500 and 400°C, respectively, by Esser and Eusterbrock (6) on Au, Ag, Cu, and Al from room temperature to the neighbourhood of the melting points and by Austin (7) on Au in the same range. Nix and MacNair have published extensive tables of direct observations from which we have obtained the values in the tables by interpolation and transformation from linear to volume expansion. Esser and Eusterbrock have published smoothed values for every fiftieth degree and Austin for every hundredth degree.

E_{vib} is for high temperatures calculated by equation (2) with the values of E_z taken from the previous paper and introduced in the headings of the tables. For low temperatures the values of E_{vib} are taken directly from the tables of the previous paper.

Table 3. Thermal expansion of solid *Cu*.

Experimental data from Nix and McNair (N. M.) and Esser and Eusterbrock (E. E.).
$E_z = 602$, $A_I = 2750$, $H_I = 4950$, $A_{II} = 168000$, $H_{II} = 19000$ cal/mole.

°K	$\frac{V-V_z}{V_0} \times 10^5$		$0.865\ E_{\mathrm{vib}}$	$1.82\ E_I$	$\frac{10^5}{H_{II}} \times E_{II}$	$\frac{\Delta V}{V_0} \times 10^5$ obs − cal
	N. M.	E. E.				
100	160		138			+ 22
150	345		330			+ 15
200	563		555			+ 8
250	784		794			− 10
273	910	910	908	1		+ 1
323	1167	1163	1157	3		+ 5
373	1402	1421	1410	7		− 6
423	1679	1684	1664	15		+ 3
473	1946	1951	1922	28		− 1
523	2211	2223	2177	46		− 6
573	2495	2503	2434	70		− 5
623	2792	2787	2699	98		0
673	3079	3077	2950	134		− 6
723	3381	3373	3207	169		+ 1
773	3687	3676	3465	209	4	+ 3
823		3986	3723	255	8	0
873		4302	3981	302	16	+ 3
923		4626	4239	353	29	+ 5
973		4950	4496	402	48	+ 14
1023		5296	4754	455	78	+ 9
1073		5643	5012	510	122	− 1
1123		5997	5270	566	180	− 19
1173		6361	5527	619	244	− 29
1223		6733	5785	675	358	− 85
1273		7115	6043	730	488	−146

E_I and E_{II} are calculated by means of equations (4) and (5), with the empirical values of A_I, H_I, A_{II}, and H_{II} from the earlier paper (2) shown in the headings of the present tables.

The empirical constants a and b are determined by trial and successive approximations. The values of V_z are obtained from extrapolations to $E_{\mathrm{vib}} = 0$. The last columns of the tables show the differences between the mean values of $(V - V_z)/V_0$ from the different series of measurements and the sum of the three terms on the right side of equation (6). The periodicity of these errors, especially marked in the table for Ag, are partly due to the fact that the expansion values are taken from results smoothed by the use of power series of T.

Close to the melting points the observed values are definitely smaller than the calculated ones. This discrepancy cannot be satisfactorily removed by introducing, according to Eshelby (3), a factor smaller than unity in the vacancy term of equation (6). There is perhaps a possibility that the specimens have yielded to the slight pressure of the measuring arrangements and it is useless to discuss details concerning the ranges below the melting points until the question is made quite clear on the experimental side.

The proportionality constants a, b, and $1/H_{II}$ of equation (6) for the relative

Table 4. Thermal expansion of solid *Al.*

Experimental data from Nix and MacNair (N. M.) and Esser and Eusterbrock (E. E.).
$E_z = 730$, $A_I = 4040$, $H_I = 4720$, $A_{II} = 89000$, $H_I = 13200$ cal/mole.

°K	$\frac{V - V_z}{V_0} \times 10^5$		$1.21\, E_{vib}$	$2.4\, E_I$	$\frac{10^5}{H_{II}} \times E_{II}$	$\frac{\Delta V}{V_0} \times 10^5$ obs − cal
	N. M.	E. E.				
100	154		139			+ 15
150	376		370			+ 6
200	656		658			− 2
250	971		979			− 8
273	1125	1125	1134	2		− 11
323	1484	1480	1475	6		+ 1
373	1842	1845	1823	17		+ 4
423	2202	2220	2176	36		− 1
473	2588	2606	2531	64	1	+ 1
523	2980	3005	2889	104	3	− 3
573	3411	3418	3250	154	10	+ 1
623		3845	3611	214	24	− 3
673		4289	3971	285	52	− 19
723		4750	4332	363	102	− 47
773		5229	4692	449	181	− 93
823		5728	5053	540	301	− 166
873		6248	5414	655	473	− 294

Table 5. Empirical proportionality constants to equation (6).

	$10^5 \times a$	$10^5 \times b$	$10^5/H_{II}$
Au	0.702	1.65	4.3
Ag	0.97	1.60	3.6
Cu	0.865	1.82	5.3
Al	1.21	2.40	7.6

expansions connected with the vibrational energy, the energy of the primary defects, and the energy of the vacancies, respectively, are put together in Table 5. These constants are of the same order of magnitude but still markedly different. An interesting observation is that b is about the double of a. Now the first term in equation (6) could also be written $2\,a\,U_{vib}$ where U_{vib} is the potential half of E_{vib}. This means that the proportionality factor between thermal expansion and potential energy is about the same for vibrations and primary defects.

5. The thermal expansion illustrating the separate contributions from vibrations and defects

For the range of temperature below and not too high above room temperature we can in equation (6) omit the last term due to the vacancies and introduce the value of E_{vib} from equation (3). Starting from 0°C with $T = T_0$, $V = V_0$, $E_{zr} = E_{zr0}$, and $E_I = E_{I0}$, we obtain the equation

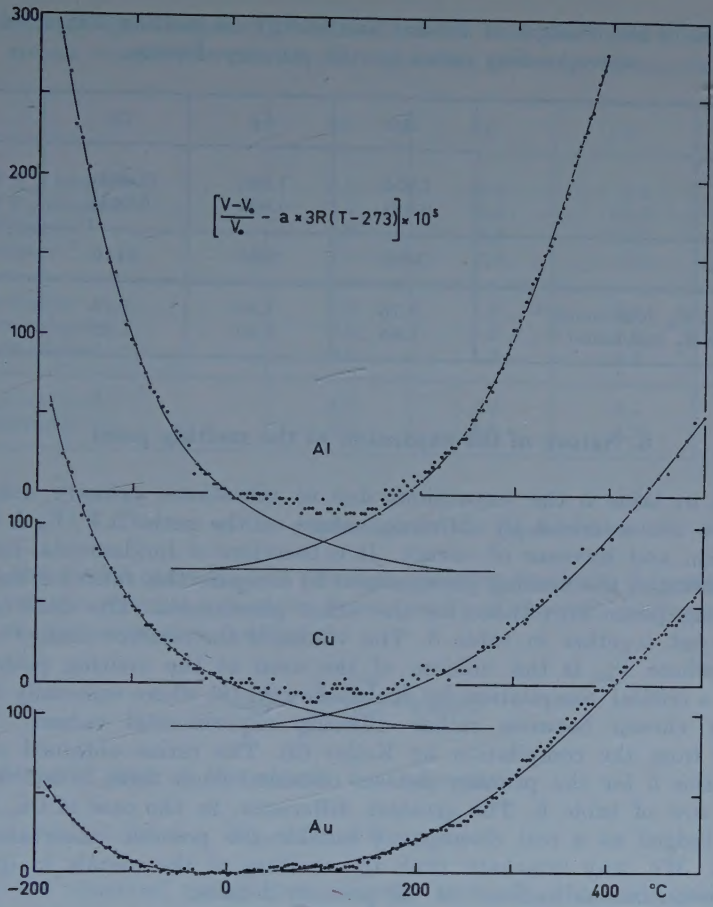

Fig. 1. Separation of contributions to the thermal expansion from vibrations and defects. Data calculated from the results of Nix and MacNair.

$$\frac{V-V_0}{V_0} - a\,3\,R\,(T-T_0) = a\,(E_{zr}-E_{zr0}) + b\,(E_{\mathrm{I}}-E_{\mathrm{I}0}). \tag{7}$$

Nix and MacNair have published detailed series of observations covering the range of temperature where the residual zero-point energy decreases to zero and the structural energy E_{I} increases from zero. Values of the expression on the left side of equation (7) derived from their measurements on Au, Cu, and Al and the values of the empirical constant a from table 5, are introduced in figure 1. For Al and Cu the two terms on the right side of equation (7) overlap. For Au the two contributions are well separated. There is a range of temperature on both sides of room temperature where the expansion coefficient of Au is practically constant and equal to $a\,3\,R$.

Table 6. Ratios of the changes of volume and energy on melting compared with the corresponding ratios for the primary defects.

	Au	Ag	Cu	Al
V_{ms}/V_0	1.055	1.065	1.068	1.053
$\Delta V_m/V_{ms}$	0.051	0.038	0.0415	0.060
ΔE_m cal/mole	3060	2690	3110	2500
$10^5 \Delta V_m/V_0 \Delta E_m$ (cal/mole)$^{-1}$	1.76	1.50	1.42	2.52
$10^5 \Delta V_I/V_0 \Delta E_I$ (cal/mole)$^{-1}$	1.65	1.60	1.82	2.40

6. Nature of the expansion at the melting point

As shown in table 5 the expansions due to vibrations, primary defects, and vacancies are characterized by differing values of the ratio $\Delta V/V_0 \Delta E$ of relative expansion and increase of energy. It is therefore of fundamental interest for an understanding of the melting phenomenon to compare this ratio for the changes at the melting point with those for the other phenomena. The data for a comparison are put together in table 6. The values of the relative change of volume $\Delta V_m/V_{ms}$, where V_{ms} is the volume of the solid at the melting point, are all taken from a critical compilation by Kubaschewski (8) where especially the ΔV_m-values were chosen between rather differing experimental values. The heat of fusion is from the compilation by Kelley (9). The ratios obtained come very near the ratios b for the primary defects obtained from table 5, and introduced in the last row of table 6. The greatest difference, in the case of Cu, cannot at present be judged as a real discrepancy outside the possible uncertainty of the experiments. We may conclude that the melting of the metals in question is mainly a discontinuous increase of the primary defects.

Another interesting question that now presents itself is to what extent the liquid state is saturated as to primary defects. The energy of formation of primary defects gives the change of heat when one mole of atoms passes over from the undisturbed lattice to the defects and is obtained from measurements in a range of temperature where the concentration of defects is still small. It seems probable that H_I will decrease at higher concentrations and that the observed H_I therefore constitutes an upper limit for the heat of saturation. The ratio

$$\varkappa = \frac{E_{Im} + \Delta E_m}{H_I} \tag{8}$$

where E_{Im} is the energy due to primary defects just below the melting point, and ΔE_m the heat of fusion, therefore means a lower limit for the degree of saturation. From the data given above we obtain for Au, Ag, Cu, and Al $\varkappa = 0.77$, 0.66, 0.72, and 0.60, respectively. We conclude that these metals are rather highly (perhaps fully) saturated with respect to the primary defects in the liquid state.

Table 7. Ratios of the changes of structural volume and structural energy in liquid metals compared with the corresponding ratios for vacancies.

	Au	Ag	Cu	Al
$10^5\, dV/dT\, V_{mf}$ (degree)$^{-1}$	6.9	10.5	9.5	12.2
$10^5\, dV/dT\, V_0$ (degree)$^{-1}$	7.7	11.6	10.6	13.6
$10^5\, a\, 3R$ (degree)$^{-1}$	4.2	5.8	5.2	7.2
$10^5\, \alpha_{\mathrm{str}}$ (degree)$^{-1}$	3.5	5.8	5.4	6.4
C cal/mole degree	7.0	7.3	7.5	7.0
γT_m cal/mole degree	0.2	0.2	0.2	0.3
C_{str} cal/mole degree	0.8	1.2	1.3	0.7
$10^5\, \alpha_{\mathrm{str}}/C_{\mathrm{str}}$ (cal/mole)$^{-1}$	4.3	5.0	4.1	8.9
$10^5/H_{\mathrm{II}}$ (cal/mole)$^{-1}$	4.3	3.6	5.3	7.6

7. Nature of the expansion in the liquid state

Also for the liquid state it is, in principle, possible to obtain information about the nature of the thermal expansion from a study of the ratio between the structural part of the expansion coefficient

$$\alpha_{\mathrm{str}} = \frac{1}{V_0}\frac{dV}{dT} - a\,3RT \tag{9}$$

and the structural part of the atomic heat capacity

$$C_{\mathrm{str}} = C - 3R - \gamma T_m \tag{10}$$

where C is the observed molar heat capacity and γT_m the heat capacity of the free electrons at the melting point. Though the accuracy of the determinations of dV/dT and C for the liquid metals are still very unsatisfactory we have for a rough orientation collected the available data in table 7. The relative changes of volume per degree $dV/V_{mf}dT$, where V_{mf} is the volume of the liquid at the melting point, are taken from the compilation by Kubaschewski (8) and the heat capacity in the liquid state from the compilation by Kelley (9). The values used for γ are the same as in the previous paper (2). The last line is taken from the last column of table 5.

From the last two lines of the table we see that the ratio between the changes of volume and heat with temperature is of the same order for the liquid state as for the formation of vacancies. In fact the uncertainty of the compiled data is such that the ratios may well be identical. We conclude that the structural part of the thermal expansion of these liquid metals is mainly due to the formation of vacancies. This is in good agreement with our earlier conclusions that the liquids are already rather saturated as to primary defects. The concentration of vacancies remains low high above the melting point.

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